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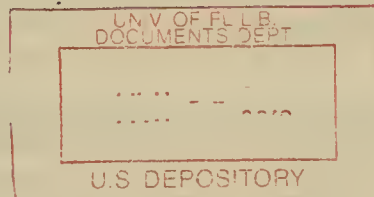
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THE ISOTOPIC CONSTITUTION OF LANTHANUM AND CERIUM

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## THE ISOTOPIC CONSTITUTION OF LANTHANUM AND CERIUM

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### ABSTRACT

The isotopic abundances of lanthanum and cerium have been determined by means of a mass spectrometer. In addition to the known lanthanum isotope of mass 139, a new isotope of mass 138 and abundance 0.089% has been discovered. Since this isotope is isobaric with two neighboring stable isotopes it should be radioactive. This activity was observed and the half-life found to be approximately  $2 \times 10^{10}$  years. Upper limits for the non-existence of other lanthanum isotopes were determined. The abundance of cerium isotopes of masses 136, 138, 140, and 142 were shown to be 0.193%, 0.250%, 88.48%, and 11.07%, respectively. Upper limits for the non-existence of other cerium isotopes were determined.

### INTRODUCTION

In view of the fact that all previous measurements of rare earth isotopic constitution have been made photometrically, it was decided to repeat these measurements, using electrometric methods. The determination of isotopic abundances by measuring positive ion currents eliminates several of the difficulties inherent in obtaining these abundances from the relative blackening of a photographic plate. The usual photometric method is to relate isotopic abundances to optical densities of mass spectra lines by means of a density curve.

The methods of printing standard intensities are liable to introduce errors if they are made by X rays, light, different ions from those examined, or by ions of different velocity. Even though these intensity marks agree with a H - D curve, the slope is dependent on the method used in printing the standard intensities. This leads to discriminations dependent upon isotopic abundance. In addition, errors may arise due to the fact that different isotopes traverse different paths in a spectrograph. Measurements of the isotopic constitution of lanthanum and cerium, together with upper limits for the non-existence of possible neighboring isotopes of these elements, are given in this paper.

### APPARATUS

The mass spectrometer used in this investigation was a Nier-type 60° six-inch radius of curvature, single focusing mass spectrometer.<sup>1</sup> Ions of the elements studied were obtained by heating their oxides on a tungsten filament. The samples were placed on the filament in nitric acid solution and upon heating, these reverted to the oxide. No organic binder was used. Ion emission began at approximately 1000°C. The ions formed were collimated into an ion beam of 2000 volts energy by the collimating plates of the source and directed normally into a wedge-shaped magnetic field. This magnetic field resolved the ion beam into its various mass components and refocused a beam of one mass through the collector slit to a collector plate. The collector plate was surrounded by an electron-repelling field of 22.5 volts, so that secondary electrons formed at the collector plate by positive-ion bombardment could not leave that plate. Ion currents were measured by a vibrating reed electrometer.<sup>2</sup> The electrometer output was recorded on a Brown Elektronik Strip Chart Recorder so that permanent records of peak shapes and intensities were obtained. Succeeding isotopes were focused on the collector by an automatic, continuous variation of the analyzer magnetic field.

The pumping system consisted of a two stage, glass mercury diffusion pump backed by a Welch Duo-Seal fore pump. A liquid air trap was used between the diffusion pump and the mass spectrometer tube to trap out vapors. The operating pressure in the tube was about  $3 \times 10^{-7}$  mm Hg as measured by an ionization gauge.

## DISCUSSION OF OBSERVATIONS

In discussing corrections which must be applied to the observed abundances, possible preferential emission of the lighter mass ions due to their higher thermal velocities must be considered. Theoretically, evaporation from the liquid phase gives a change in the abundance ratio of two isotopes proportional to the square root of the ratio of the masses. This separation is attained only if there is perfect mixing at the surface of the liquid. In the solid phase, there is little mixing, and so there should be little separation. Since the material on the filament was not in the molten state, no mass discrimination was expected. To test this hypothesis, isotope ratios were taken from the time emission began until the sample was completely evaporated from the filament. If any such mass discrimination took place, the last determinations would have given large ratios of heavier masses than did the first. No such effect was noted and hence it was concluded that no vapor pressure discrimination took place.

Another error would be introduced if the ratio of ions to atoms emitted from the filament were dependent on the mass of the isotope. However, since the efficiency of ionization in this type of source depends on the ionization potential and not on the mass, it is concluded that this effect is negligible.

Possible space charge discriminations near the filament are negligible because the emission from the filament is temperature-limited rather than space-charge limited.

With this ion source, the electron focusing magnet usually used on the source of Nier-type mass spectrometers was unnecessary and was omitted. Thus no magnetic isotope discriminations could have occurred in the source.<sup>3</sup>

The condition for no discrimination between light and heavy ions in their passage through a mass spectrometer is that the ion paths for different ions be identical. This condition was fulfilled in these measurements by bringing different masses to focus at a fixed point by varying the analyzer magnetic field and keeping ion energy constant.

Inaccuracy in the current measuring system could have been caused by non linearity of the  $2 \times 10^{10}$  ohm input resistor of the vibrating reed electrometer or by non-linearity of response through the electrometer and the recorder. However, measurement showed the input resistor to be constant to better than 1% in the range of 1 millivolt to 10 volts, the range used in these experiments. Measurement of the linearity of the amplifying and recording system showed its response to be linear to within 0.2%. Thus all systematic errors are less than 1%, and to this degree of accuracy the observed peak heights are proportional to isotopic abundances.

## EXPERIMENTAL RESULTS

### Lanthanum Abundances

$\text{La}_2\text{O}_3$  heated on a tungsten filament gave rise to  $\text{LaO}^+$  ions. A typical recorder curve of these ions is shown in Figure 1. Peaks of masses at 154, 155, 156, and 157 are present. The sensitivity of the recorder at mass 155 is less by a factor of 200 than the sensitivity over the rest of the curve. The peaks at 155, 156, and 157 are due to  $\text{La}^{139}\text{O}^{16}$ ,  $\text{La}^{138}\text{O}^{17}$ , and  $\text{La}^{139}\text{O}^{18}$  ions, respectively. Calculation of abundance of these peaks gives values for the abundance of the oxygen isotopes of 99.752%  $\text{O}^{16}$ , 0.041%  $\text{O}^{17}$ , and 0.207%  $\text{O}^{18}$ . These results agree with those of Murphey<sup>4</sup> within 2% so that within this limit these peaks are ascribed entirely to  $\text{La}^{139}\text{O}^{16}$ ,  $\text{La}^{139}\text{O}^{17}$ , and  $\text{La}^{139}\text{O}^{18}$ . Thus, if there are any  $\text{La}^{140}$  and  $\text{La}^{141}$  isotopes they must be less than 2% of the height of the last two peaks. The ion at mass 154 we ascribe to the oxide of a new isotope,  $\text{La}^{138}$ .



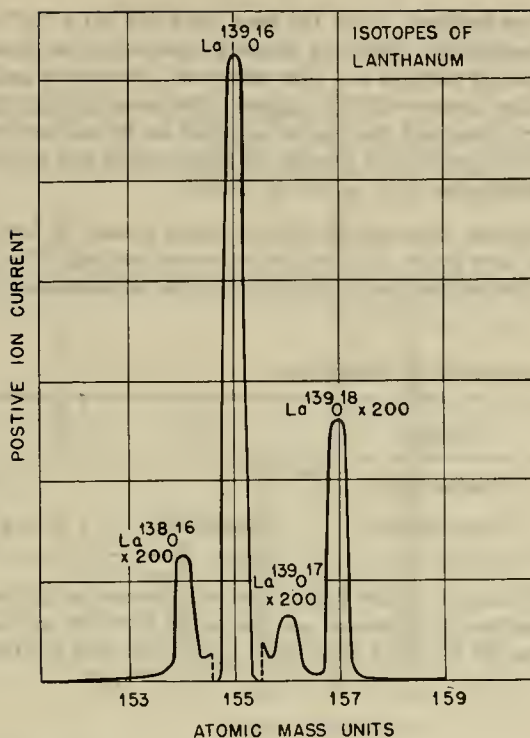


Figure 1. Recorder tracing of isotopes of lanthanum as observed in the  $\text{LaO}^+$  position. The peak at mass 155 is recorded at one two-hundredth of the sensitivity used for the rest of the tracing.

The possibility that this peak is due to another element has been ruled out by the following considerations: If the peak at mass 154 were due to an impurity of some other element in lanthanum, this impurity would probably not be of the same intensity in various samples. We observed the 154 peak in two specially purified samples, a sample of spectrographically pure  $\text{La}_2\text{O}_3$  prepared by Professor Rolla and obtained from Adam Hilger, Inc., as Laboratory Number 6781, and a second sample of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  obtained from Kahlbaum. Within 1% no difference could be detected in the ratio of the 154 to 155 peaks in these two samples. Further evidence that the mass 154 is not due to an element other than lanthanum is provided by the characteristics of surface ionization. For example, if a mixture of lanthanum and cerium is placed on the filament, the ratio of the cerium to the lanthanum increases strongly with time due to the fact that lanthanum ions are emitted at a lower temperature than the cerium ions. This effect is present in varying degrees between lanthanum and any other element which emits positive ions from a tungsten filament. No variation with time of the 154 to 155 ratio could be detected. This indicates that the 154 peak belongs to lanthanum. A final argument that the 154 peak is due to  $\text{La}^{138}\text{O}^{16}$  is based on a consideration of the other elements which could conceivably give rise to this peak. These are barium, cerium, samarium, and gadolinium; since  $\text{O}^{15}$  is known to exist to less than one part in one hundred thousand, this could not be the cause of this peak. A barium peak at mass 154 would have to be  $\text{Ba}^{138}\text{O}^{16}$ . Since barium does not emit as  $\text{BaO}^+$ , but rather as  $\text{Ba}^+$  and because the  $\text{Ba}^{137}\text{O}^{16}$  line was not observed at mass 153, this possibility

is ruled out. Cerium is ruled out because, if the 154 peak were due to  $\text{Ce}^{138}\text{O}^{18}$ , the 156 peak due to  $\text{Ce}^{140}\text{O}^{18}$  would have to be 700 times larger than was actually observed. The possibility of CeN is ruled out by the fact that no charged nitrides are ever observed. Samarium and gadolinium are likewise ruled out because their other isotopes did not appear. The possibility of dissociation of LaOH between the accelerating electric field and the magnet is ruled out by the fact that LaOH was not present, and that no similar line appears with cerium. It must, therefore, be concluded that the isotope of mass 138 exists in lanthanum as it occurs in nature.

The results of this investigation, together with the previous results of Aston<sup>5</sup>, are summarized in Table 1. The results are the average of forty separate determinations. The uncertainty tabulated is the mean deviation of these determinations. Any other isotope of lanthanum is present to less than 0.002%.

Table 1. Isotopic constitution of lanthanum.

Reference	Method	138	139
Aston <sup>5</sup>	Photometric	-	100 per cent
Present work	Electrometric	$0.089 \pm .001$	$99.911 \pm .001$

Calculation of the chemical atomic weight from these abundances using Dempster's<sup>8</sup> value of  $-3.2 \times 10^{-4}$  for the packing fraction of lanthanum and the factor 1.000275 in converting from physical to chemical atomic weight gives 138.92 which is in exact agreement with the international chemical atomic weight of 138.92.

#### Lanthanum Activity

Lanthanum<sup>138</sup> is an unusual isotope in that it occurs between two stable isobars,  $\text{Ba}^{138}$  and  $\text{Ce}^{138}$ . This occurs at only two other places in the atomic table, namely in the case of  $\text{K}^{40}$  and  $\text{Lu}^{176}$ . It is similar to these isotopes also in that its nucleus contains an odd number of protons and an odd number of neutrons. No naturally occurring odd-odd isotopes are stable heavier than  $\text{N}^{14}$ . Both  $\text{K}^{40}$  and  $\text{Lu}^{176}$  are known to be radioactive with half-lives of  $4 \times 10^8$  years and  $7.3 \times 10^{10}$  years, respectively. In view of the similarity between  $\text{La}^{138}$  and these two isotopes, it was thought that the  $\text{La}^{138}$  would probably be active, and a search for this activity was carried out, using a counter with a 3 mg/cm<sup>2</sup> window. An activity of approximately 250 Kev consisting of beta rays was found to be present. The specific activity was also measured and assuming this activity to be due to the disintegration of  $\text{La}^{138}$ , the half-life of this activity is approximately  $2 \times 10^{10}$  years.

#### Cerium

Cerium was first studied by Aston<sup>5</sup> and shown to consist mainly of isotopes 140 and 142. Later Dempster<sup>7</sup> found two rare isotopes at masses 136 and 138. A typical recorder curve for cerium obtained with our apparatus is shown in Figure 2. The mass 156 was recorded at sensitivity 100 times less, and mass 158 recorded at sensitivity 20 times less, than the sensitivity used over the rest of the curve. Only the masses 152, 154, 156, 157, 158, 159, and 160 were observed. These were due to the ions  $\text{Ce}^{138}\text{O}^{18}$ ,  $\text{Ce}^{138}\text{O}^{18}$ ,  $\text{Ce}^{140}\text{O}^{18}$ ,  $\text{Ce}^{140}\text{O}^{17}$ ,  $\text{Ce}^{142}\text{O}^{18}$ ,  $\text{Ce}^{140}\text{O}^{18}$ ,  $\text{Ce}^{142}\text{O}^{17}$ , and  $\text{Ce}^{142}\text{O}^{18}$ , respectively. The cerium isotopic abundances, corrected for the rare oxygen isotopes are given in Table 2. These results are the average of forty separate determinations. The uncertainty tabulated is the mean deviation of these determinations.

No peaks other than those due to the oxides of these four cerium isotopes formed with  $\text{O}^{18}$ ,  $\text{O}^{17}$ , and  $\text{O}^{16}$  could be detected. The following upper limits for possible cerium isotopes of neighboring mass were obtained: 134, 135, and 137, less than 0.004%; 139 and 141, less than 0.02%; 143, 144, 145, and 146, less than 0.004%.

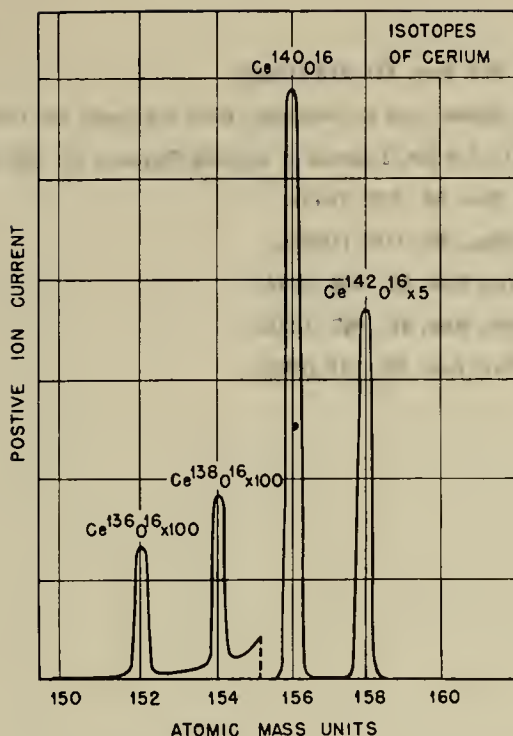


Figure 2. Recorder tracing of isotopes of cerium as observed in the  $\text{CeO}^+$  position. The peak at mass 156 is recorded at one-hundredth the sensitivity, and the peak at 158 at one-twentieth the sensitivity, used at masses 152 and 154.

Table 2. Isotopic constitution of cerium.

Reference	Method	136	138	140	142
Aston <sup>5</sup>	Photometric	-	-	89.0	11.0
Dempster <sup>7</sup>	Photometric	< 1%	< 1%	-	-
Cohen <sup>8</sup>	Electron multiplier	~ 0.18	~ 0.22	-	-
Present work	Electrometric	$0.193 \pm .005$	$0.250 \pm .005$	$88.48 \pm .10$	$11.07 \pm .10$

Calculation of the chemical atomic weight from these abundances, assuming a packing fraction of  $-3.0 \times 10^{-4}$ , and the factor 1.000275 in converting from physical to chemical atomic weight, gives 140.10, which is in agreement with the international chemically determined atomic weight of 140.13.

We wish to express our appreciation to Prof. A. J. Dempster for many helpful discussions.

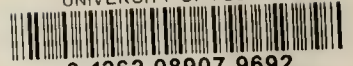
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